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Combined EPR and DFT study of the copper(II) complexes with *N*-phosphoryl thioureas

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Abstract

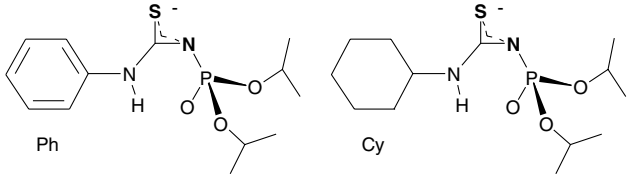
Copper(II) bis-complexes with *N*-phosphoryl thioureas, $RN'HC(S)NP(O)(OPr^i)_2^-$ {R = phenyl (**I**), cyclohexyl (**II**)}, have been obtained and investigated in liquid and frozen toluene solutions. Equilibria between *trans*-S,N and *cis*-S,N-isomers have been revealed and described by EPR method. In contrast to more usual S,O-forms, *trans*-S,N-isomers demonstrate large superhyperfine splitting from N and P atoms simultaneously. From EPR spectra anisotropic hyperfine, superhyperfine, and *g*-tensor parameters obtained and the symmetry of the metal ion surrounding analyzed. Rhombic anisotropy of copper(II) hyperfine and axial symmetry of N and P superhyperfine splitting resolved. Structural, hydrodynamic, and magnetic characteristics of the complexes established experimentally were supported by DFT calculations. According to EPR and DFT studies, tetrahedral distortion is higher in *cis*-S,N than in *trans*-S,N forms for steric reasons and slightly higher in **I**(S,N-*trans*) isomer than in **II**(S,N-*trans*) one due to the electron-donating effect of cyclohexyl substituent. The domination of S,N- over S,O-coordination is explained by the effects of the crystal field stabilization and the formation of the intramolecular hydrogen bonds.

Keywords: EPR; DFT; Hyperfine structure; Nitrogen and phosphorus superhyperfine coupling; Copper complexes; Phosphoryl thioureas

1. Introduction

Copper(II) complexes with *N*-(thio)phosphoryl thioureas containing an unique pentade X–P–N–C–X in the chelate rings (where X is O or S) are very attractive to study because of possibility to relate the alterations in chelate ring atoms and the substituents at P and C atoms with the changes of dynamic and magnetic properties [1–3]. In previous X-ray and EPR studies [1–3] complexes of copper(II) with *N*-(thio)phosphoryl thioamides $\{RC(S)NHP(X)(OPr^i)_2$, X = S, O; R = Ph, etc.$\}$ have shown to form S,S- or S,O-coordinated molecules with six-member chelates tetrahedrally distorted from plane.

In this work we have discovered that change from $RC(S)NHP(X)(OPr^i)_2$ to $RN'HC(S)NHP(O)(OPr^i)_2$ {R = Ph (phenyl), Cy (cyclohexyl)} leads to an unusual coordination through S and N atoms and gives rise to the square-planar four-member metallochelates with $RN'HC(S)NP(O)(OPr^i)_2^-$.



An interesting feature of the compounds obtained in this work is that they exhibit resolved phosphorus superhyperfine splitting in addition to nitrogen one, what

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